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Survival of gas phase amino acids and nucleobases in space radiation conditions

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Abstract. We present experimental studies on the photoionization and photodissociation processes (photodestruction) of gaseous amino acids and nucleobases in interstellar and interplanetary radiation conditions analogs. The measurements have been undertaken at the Brazilian Synchrotron Light Laboratory (LNLS), employing vacuum ultraviolet (VUV) and soft X-ray photons. The experimental set up basically consists of a time-of-flight mass spectrometer kept under high vacuum conditions. Mass spectra were obtained using photoelectron photoion coincidence technique. We have shown that the amino acids are effectively more destroyed (up to 70-80%) by the stellar radiation than the nucleobases, mainly in the VUV. Since polycyclic aromatic hydrocarbons have the same survival capability and seem to be ubiquitous in the ISM, it is not unreasonable to predict that nucleobases could survive in the interstellar medium and/or in comets, even as a stable cation.

Keywords. methods: laboratory, molecular data, astrochemistry, astrobiology

1. Introduction

The search for amino acids and nucleobases (and related compounds) in the interstellar medium/comets has been performed at least in the last 30 years, but unfortunately it was not successful yet (e.g. Brown et al. 1979; Simon & Simon, 1973). However, recently some traces (upper limits) of simplest amino acid, glycine (NH_2CH_2COOH) were observed in the comet Hale-Bopp (Crovisier et al. 2004) and in some molecular clouds associated with the star forming regions (Kuan et al. 2003a) but these identifications have yet to be verified (Snyder et al. 2005; Cunningham et al. 2007). Despite no direct detection of nucleobases in comets or in the molecular clouds, some of their precursors molecules like HCN, pyridines, pyrimidines and imidazole were been reported in the Vega 1 flyby of comet Halley (Kissel & Krueger, 1987) and have been searched in the interstellar medium (Kuan et al. 2003b).

The search for these biomolecules in meteorites, on the contrary, has been revealed an amazing number of proteinaceous and non-proteinaceous amino acids, up to 3 parts per million (ppm) (e.g. Cronin 1998 and references therein), and some purine and pyrimidine based nucleobases up to 1.3 ppm (e.g. Stocks & Schwartz 1981 and references therein). This dichotomy between the carbonaceous chondrites meteorites and interstellar medium/comets chemistry remains a big puzzle in astrochemistry filed and in the investigation about the origin of life.

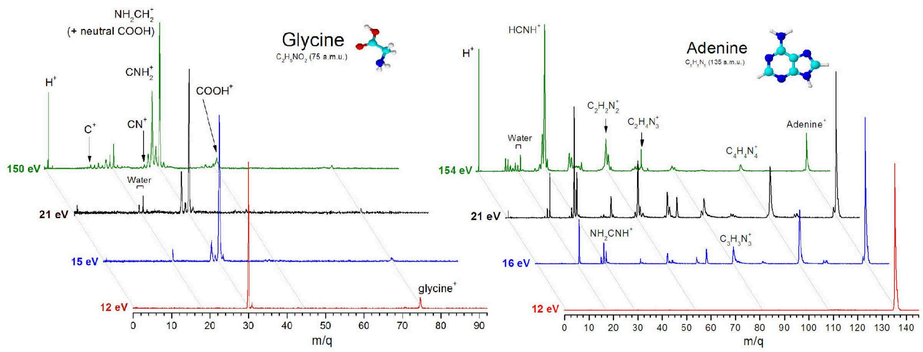

Figure 1. Time-of-flight mass spectra of gaseous amino acid glycine and nucleobase adenine recorded at different photon energies at VUV (12-21 eV) and at soft X-ray ($\sim$ 150 eV) ranges.

The goal of this work is to review some experimental gas-phase photoionization and photodissociation studies of amino acids and nucleobases induced by vacuum ultraviolet (VUV) and soft X-ray photons, obtained recently by our group (Lago et al. 2004; Coutinho et al. 2005; Marinho et al. 2006; Pilling et al 2007c). A possible direction on the different survivability of these biomolecules on astrophysical environments are given.

2. Experimental methodology and results

In an attempt to simulate the stellar/solar VUV and soft X-ray flux we have used a synchrotron radiation as a light source. The experiments were performed at the Brazilian Synchrotron Light Laboratory (LNLS), employing harmonic free VUV photons (Cavasso-Filho et al. 2007) and soft X-ray photons from the toroidal grating monochromator (TGM) beamline. The emergent photon beam flux was recorded by a light sensitive diode. Briefly, the radiation ($\sim 10^{12}$ photons s^{-1}) from the beamline perpendicularly intersect the vapor-phase sample at the center of the ionization region inside a high vacuum chamber (Boechat-Roberty et al. 2005; Pilling et al. 2006). Mass spectra were obtained using photoelectron photoion coincidence (PEPICO) technique (Pilling et al 2007a; 2007b and references therein).

In Fig. 1 we have shown the time-of-flight mass spectra of the fragments released from the amino acid glycine and the nucleobase adenine, recorded at different photon energies over the VUV (12-21 eV) and soft X-ray ($\sim$ 150 eV) ranges. As a general rule, even at low photon energy, the amino acids have only a small contribution ($\lesssim 10\%$) or even they were not detected, a consequence of their high photodestruction degree. The release of the carboxyl group (COOH) as a neutral or cationic species, depending on the amino acid, is one of the most import dissociation channels (see also Jochims et al. 2004). The nucleobases have shown a higher molecular stability in comparison with the amino acids ones. For these molecules, the parent ions remain relatively strong over all the studied VUV photon energy range. In all spectra, as the photon energy increases also increase the fragmentation profile, as expected. Some minor contamination of water was observed in the spectra, which reflects the high hydrophilic character of the samples.

In the previous studies of photodissociation of nucleobases (e.g. Jochims et al. 2005; Schwell et al. 2006) at the VUV photon energy range the authors have identified some important photodissociation channels as well the HNCO loss by thymine and uracil and HCN loss by adenine. As pointed by Pilling et al. (2007c), in the case o adenine, the

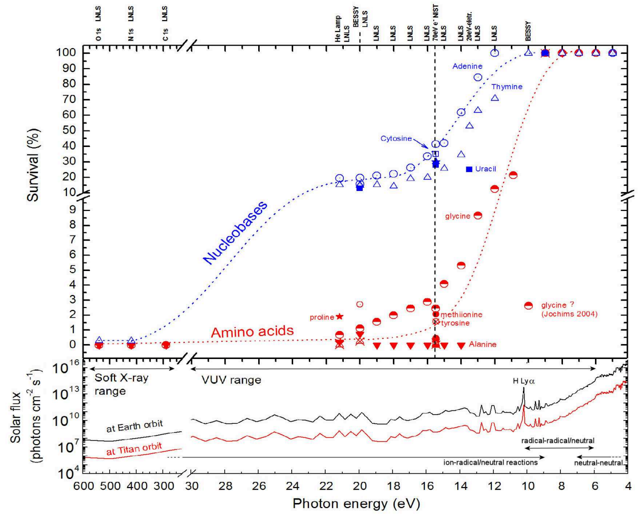

Figure 2. Comparison between the survival (photoresistence) of different amino acids and nucleobases due to ionizing radiation field in the VUV and soft X-ray. The solar photon flux at Earth and Titan orbit (adapted from Gueymard 2004). See details in text.

neutral HCN may represent as much as 40% of its photodissociative channels. The ion $HCNH^+$ is another largely photoproduced fragment from both amino acids and nucleobases.

A comparison between the survival of different nucleobases and amino acids due to ionizing radiation field from 4 to 600 eV is given at Fig. 2. Our data is represented by LNLS labels. The literature data were gather mainly from the NIST database and Jochims et al. (2004; 2005). The amino acids are effectively more destroyed by VUV stellar/solar radiation than the nucleobases. The higher resistance of nucleobases to the ionizing photons may be associated with the presence of the hetero-cyclic structure and unsaturated bonds.

For comparison, we also present in the bottom panel of Fig. 2, the solar photon flux at ultraviolet and soft X-rays at Earth and Titan orbit (adapted from Gueymard 2004). The different photochemical domains are also given. According to the detailed review of Schwell et al. (2006), the photoabsorption cross section of these molecules is higher in VUV as compared to the mid-UV (< 6 eV). In particular all molecules, absorb strongly at 10.2 eV, where the intense Lyα (10.2 eV) stellar/solar emission is located. Most of the small biomolecules studied have first ionization energies (IE) below this energy, making photoionization phenomena an important issue to study. Since most of the amino acids has the first AE below 10.2 eV, the stellar/solar hydrogen Lyα has a great influence on their molecular survival. This is not observed in the case of nucleobases which the first AE occurs at energy above the hydrogen Lyα, where the photon flux is about 2 orders of magnitude lower (in the case of Sun).

3. Conclusion

We have shown that the amino acids are effectively more destroyed by stellar radiation than the nucleobases, mainly at VUV spectral range where the differences reach up 70-80 % decreasing to high-energy photon range, corroborating other experimental results given in the literature. The nucleobases are able to form a stable cation in gas phase and since polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic nitrogen-rich

hydrocarbons (PANHs) have the same capability and seem to be ubiquitous in the ISM (Allamandola et al. 1986), it is not unreasonable to predict that aromatic nucleic acid bases could survive in the interplanetary and interstellar medium.

These results lead us to make an interesting question. Why we did not find nucleobases in cometary/molecular clouds radioastronomical observation since they are quite more resistant to stellar ultraviolet radiation than the detected amino acid (e.g. glycine)? Probably, the answer may be associated with the formation pathways efficiencies rather than with the detection limits and more studies over this subject are need.

Finally, a possible direction to the search of large pre-biotic molecules, as the case of amino acids and nucleobases or even for larger molecules, could be the search not for the molecules themselves, but from their photoproduced daughter species like, for example, the fragments $COOH^+$, $HNCO^+$, HCN^+ and $HCNH^+$. The abundances, derived from the radio-observation of these fragments, combined with the laboratory data (e.g. relative ion yield and photoproduction cross section) may give us a clue about the presence and the amount (upper limit) of their parent molecules.

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